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**Studies on Coating Process
for Organic/Inorganic Thin-Films
for Photovoltaics**

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Despite current policies and regulations limiting use of fossil fuel, energy-related carbon dioxide emissions around the world are projected to escalate every year. Accordingly, we confront with the environmental pollution and the greenhouse effect from which people have suffered seriously. Therefore, it is one of the most critical tasks for human being to develop novel clean and inexpensive energy sources. In the growing efforts to seek for new energy source, it is generally accepted that the solar energy is one of the most promising, available, renewable energy sources of all. In addition, the advantage of solar power is the location-free energy, portable device and inexhaustible supply. The solar cell is a photovoltaic (PV) device that converts sun light into electricity. Among all kinds of solar cells, inorganic semiconductors based solar cells have been developed very rapidly in the past decades and thus represent the most mature technology by taking up around 70% of photovoltaic markets nowadays.

Recently, organic solar cells (OSCs) have evolved as a promising alternative to high-cost silicon-based solar cells.^[1-3] For making the polymer photovoltaic cells, the spin-coating method has been widely used in fabricating a device, due to its high precision and reproducibility. However, with spin-coating, an inherent large amount of materials is wasted in the process. Moreover, the process is not compatible with roll-to-roll or large area manufacturing. Among other solution processes investigated as a replacement for

spin coating, such as screen printing, doctor blading, inkjet printing, slot-die coating to the manufactured roll-to-roll production, the spray coating is considered as one of cost-effective coating methods.^[4-8] The spray deposition technique showed high and reproducible performance despite of high-throughput deposition. Also, the spray process can allow for patterning and use of insoluble organic materials.

However, spray coating also have some fundamental problems. The active layer formed by loosely-linked droplets has pinholes which decreases device performance by having a lower fill factor (FF). This limitation would be partially solved by increasing the thickness of active layers by controlling the spray time and concentration of active layer materials in solution. Considering that the amount of absorbed solar radiation depends on the device thickness, a thicker active layer can promote better device performance. However, thicker devices are also associated with high series resistance, reduction of dissociation rate of excitons, and increased recombination of charge carriers, which can degrade device performance.^[9] For the spin-coated solar cells based on poly (3-hexyl thiophene) (P3HT) and the C_{60} -derivative, (6, 6)-phenyl C_{61} -butyric acid methyl ester (PCBM), it has been reported that the most efficient performances have been obtained in devices with an active layer thickness of around 80 nm. Devices with a slow-grown active layer, however, showed optimum performance at thicknesses around 220 nm.^[9-11] Contrary to this trend of spin coated solar cells, high power conversion efficiency (PCE) in spray coated devices has been achieved with thicknesses in the range of 200-300 nm, which is already regarded as considerably thick.^[12-16] A particular research group has reported optimum PCE s at even thicker active layers (440 nm) in conventional spray coated devices.^[17] However, there has not been any further study on the dependency of

photovoltaic characteristics and surface morphology according to the thickness of the active layer in spray coated devices. It was found that the internal pinholes were densely filled up with other droplets and light absorbing become more efficient, as thickness increases. Thus, the optimum *PCE* was obtained in about 220 nm, a relatively thicker active layer when compared to the optimum thickness of spin coated devices. Furthermore, it was shown that the performance is insensitive to the thickness of the active layer in spray coated devices. This phenomenon is attributed to the internal structure and rough surface with pinholes, especially in thicker active layer above 300 nm.

Nevertheless, spray coating is still required to improve the efficiency for enlarging the usage as an alternative method. Usually, spray deposition for the preparation of the bulk heterojunction active layer with P3HT:PCBM in OSCs has been developed largely in two ways: the first method involves fast spray coating for a uniform wet layer with a high solution flow rate, and the other involves a slow spray coating process which results to a multiple pass layer obtained by controlling the contact angle with an adequate solvent and flow rate.^[18-20] However, both ways have drawbacks. It is hard for the former to scale up due to non-uniform surface and defects, while loosely-linked droplets and pinholes obstruct improvement of efficiency in the latter. For both cases, the evaporation of the solvent in the spray coating process is affected by the equilibrium between the liquid phase and the vapor phase surrounding the droplet, limiting diffusion. This accounts for the formation of a coffee ring along the initial contact line of the droplet which leads to a non-uniform morphology of the surface and a sparse active layer matrix.^[21] This consequently leads to poorly performing solar cells since it prevents the escalating and

elongating of P3HT crystals which are crucial for high efficiency, as proven by the improvements made by the thermal annealing process. Therefore, some research groups have tried new ways to avoid these inevitable problems. Green et al. reported spray deposited P3HT:PCBM films from various organic solvents with different boiling points.^[22] Recently, Park et al. showed that the fabrication of sprayed solvent over-layer method gives highly efficient devices.^[23] Furthermore, Susanna et al. presented high power conversion efficient solar cell by optimizing the parameters of the spray system, especially using a co-solvent mixture.^[24] Here, the film formation, surface topography and the morphology of active layer through additional solvent spray coating with various solvents, such as chlorobenzene (CB), chloroform (CF), ortho-dichlorobenzene (DCB) and ortho-dichloro benzene/mesitylene (DCB/Mes) were specially investigated. This additional solvent spraying immediately follows the active layer deposition by spray coating of mixed solution of P3HT:PCBM in CB that followed the spray coating of the electron-blocking layer of poly (3,4-ethylenedioxy thiophene):poly(styrene sulfonate) (PEDOT:PSS). Since the additional solvent spraying process, especially with DCB, is accompanied by a slow drying process and the reorganization of the P3HT:PCBM matrix, it effectively induces a larger crystallite of P3HT and helps overcome the non-uniform morphology of the matrix. All of the morphological changes in a P3HT:PCBM system after this process and subsequent thermal annealing resulted in improvement of photon absorption, better exciton dissociation, and more efficient and balanced transportation of free charges to the electrodes, reflected in higher values of fill factor and current density. All of this therefore corresponds to better overall efficiencies for corresponding solar cell

devices. The additional spray coating of DCB solvent resulted in the doubling of the performance, compared to conventionally sprayed devices.

To realize precise controlling and large solar cell, fine channel mist spray deposition (FCMSD) method was developed on the basis of the experimental data and characteristics of the spray coating. This FCMSD method is a simple coating method, in which the liquid solution is ultrasonically atomized and the aerosol droplets are transferred onto the substrate by carrier gas. This method is a modification of an applied version of chemical vapor deposition (CVD), which is a chemical process used to produce high-purity, high performance in the semiconductor industry for thin films.^[25-28] Recently, CVD method is also used to deposit transparent ZnO thin films.^[29-30] However, in this experiment, FCMSD method is different from CVD since the fine channel mist deposition process consists of the donor and/or acceptor spray coating by gas pressure without chemical reaction of the precursors. In this respect, the FCMSD method as an alternative screening tool for the optimum ratio of P3HT:PCBM thin film solar cell was studied. The desired ratio of donor/acceptor was reproducibly and accurately deposited on the substrate. However, with just the FCMSD method, the active layer components were poorly blended. The problem by using the additional solvent coating method to enhance the rearrangement of P3HT:PCBM components in the active layer was improved. In the screening for the optimum ratio of PCBM/P3HT, when the PCBM fraction is low, the P3HT molecule has a limitation of elongation during crystallization upon thermal annealing as shown in result of XRD and TEM. Unfortunately, poorly mixed active layer still exists after additional solvent coating and results to the 'M' curve in *IPCE*. Finally, the highest *PCE* of 1.5 % is obtained for the device with the P3HT:PCBM ratio of 1:0.88.

The FCMSD method showed the capability to screen optimum device structures compared to the other methods as roll-to-roll technique. More meaningful result about best mixing ratio of other polymers and fullerenes continuously on the basis of this result can be expected. Furthermore, it is believed that this FCMSD method can encourage the development of novel donors and acceptors in OPVs.

Through new coating process with the FCMSD technique, the critical factors to apply the three types of solar cells, which is normal, inverted and hybrid type, were investigated. The experiments were proceeded to overcome against limitations such as use of a heated substrate and difficulty of detail manipulation on process, maintaining advantages of the FCMSD method as like well-controlled mass production. Fully enough blending donor/acceptor solution is required to obtain a comparable and reproducible performance in normal type solar cell. In inverted type device, the combination of pre and post heat treatment (at 150 °C and 180 °C, respectively) induced better crystallization of ZnO. As a result, vertical distribution and trade-off between ordering of P3HT and growth of ZnO happened in the way of applying the FCMSD to hybrid solar cells directly. It is expected that this new technique will be an all-around alternative process for large scaled manufacturing production as well as various types of solar cells, keeping in mind the discussed factors. It is also believed that the novel structure and a continuous electrode can diversify module concept for connecting two adjacent solar cells.

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